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Investigations of Interactions Between Hydraulic Drag Reducing Agents and Corrosion Inhibitors

by

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ABSTRACT

This is a final report from the "Investigation of Interactions Between Hydraulic Drag Reducing Agents and Corrosion Inhibitors". Testing was done by electrochemical methods and by immersion of test coupons of AISI 1020 steel in a stagnant media that incorporated water, drag reducing agents, antifoaming agents and corrosion inhibitors. The drag reducing agents were ethoquad with either 2,6-dihydroxybenzoic acid or 3-methylsalicylic acid.

Results from the experiments with inhibited systems were compared with results obtained in the uninhibited systems. The data indicates that the corrosion current densities in systems with 3-methylsalicylic acid were reduced to about 1/100 of those observed in the uninhibited systems. This inhibitor was also effective in the systems of 2,6-dihydroxybenzoic acid. About the same amount of steel corrosion occurred in the oxygen free as in the oxygen saturated systems. Particularly effective was the inhibitor based on an amine carboxylate.

A limited testing indicated that the Ida Freeze and Alox Aqualox 225A-100 may be even better inhibitors for the systems with 3-methylsalicylic acid than the amine carboxylate based VCI-649 inhibitor.

It is proposed that the combinations of these inhibitors, i.e., Ida Freeze and Alox 225A-100 in combination with the drag reducing agent incorporating 3-methylsalicylic acid is investigated in more detail.

BACKGROUND

Water has many desirable chemical and physical properties which make it suitable for the storage of cooling capability and as an energy transfer medium. In cooling water systems, the chilled water can be readily stored in tanks with little loss of cooling capability, unlike heat storage, which is difficult to accomplish. Water is non-hazardous, readily available and cheap. Despite these desirable properties there are, however, many problems associated with using water as an energy storage and transport medium in cooling thermal energy storage and transfer systems.

Water can be extremely problematic with respect to equipment life and has a relatively low volumetric capacity for cold heat transfer. However, both these areas can be easily improved by use of ice slurry rather than chilled water for storage and transfer of cooling energy. The heat associated with phase change in ice slurry enhances the volumetric heat capacity of water about 10 times. The second aspect related to life of the metallic materials with which the heat transfer medium comes in contact in cooling systems can be managed by the use of water treatment practices and additives used in the conventional water chillers and cooling towers. However, when the cooling storage and heat transfer media also contain ice particles, these can cause friction in the pipes and develop a drag force that could lead to reduced efficiency of the transfer systems. Friction in the pipes could also lead to an increase in the deterioration of metallic surfaces exposed to the heat transfer medium. Even though the thermal storage and transfer systems operate at relatively low temperature profiles where the reaction of heat transfer medium and metal proceeds at slower rates than in systems operating at higher temperatures, the problems of corrosion, biological growth and possible solid deposition can occur just the same as in any other water utilizing systems.

The settling of deposits should not be a problem, especially in clean cooling storage and heat transfer systems in which all suspended solids and debris were properly removed prior to system start up and in which there is no corrosion. The biological growth of slime into which products of corrosion may get ingressed and lead to a more serious localized corrosion can also be controlled by use of a suitable biocide. However, the need for control of biological growth in cooling systems incorporating drag reducing agents investigated in this work has not yet been fully recognized. This control may be needed even though in some parts of the system the temperature will rise to a level detrimental to microbial life. The biofouling can occur in areas where temperatures are favourable for biological activity. In these sections of the system bacteria could attach to the walls of the pipes forming biofilms or slimes into which organic and inorganic nutrients present in the liquid would be absorbed and utilized by the microorganisms. Depending on the availability of oxygen, the bacteria involved could be aerobes or anaerobes. To prevent biofilm formation, which could lead to biologically-induced corrosion, a suitable biocide should be added to the liquid. A number of biocides would have to be tested to select one compatible with the medium and additives used in the cooling system.

The friction losses due to drag in the conduit of the cooling transfer media can be reduced and the efficiency of the process increased by employing chemical additives called drag or friction reducing agents.

Two effective drag (or friction) reducing agents have been developed by Dr. John Young's group at Saint Mary's University. These water soluble drag reducing agents, essentially quaternary ammonium salts are used as highly concentrated aqueous solutions. These solutions are suitable for making ice slurry and can be used as highly efficient cold energy storage and transportation medium.

The active corrosion in cooling storage and energy transfer systems can be prevented by the use of corrosion inhibitors.

It was the objective of this work to develop a corrosion inhibitor or inhibitors for the cold energy storage and heat transport systems incorporating the aqueous solution of drag reducing agents.

The most important requirements of such inhibitors are summarized as:

1. Compatibility with friction reducing agents.

2. Effective inhibition of corrosion.

3. Stability against temperature and oscillation in temperature.

4. Environmental acceptance.

Inhibitor evaluation can be made by a number of tests in which either weight loss, depth of pits or corrosion rates and/or corrosion currents are determined.

TESTING

The effectiveness of various inhibitors in aqueous solutions of friction reducing agents. i.e. ethoquad with either 3-methylsalicylic acid (FRA # 1) or 2,6-dihydroxybenzoic acid (FRA # 2) incorporating doses of corrosion inhibitors recommended by the suppliers of inhibitors, was evaluated by static laboratory immersion testing and by electrochemical testing.

A) Materials

1. Friction Reducing Agents (FRA)

Two friction reducing agents were supplied by Dr. John Young's group at Saint Mary's University. These included:

- Ethoquad with 3-Methylsalicylic Acid (FRA # 1)
- Ethoquad with 2,6-Dihydroxybenzoic Acid (FRA # 2)

2. Metallic Samples

The test coupon material on which the evaluation of inhibitors was made was a low carbon AISI 1020 steel sheet with nominal composition close to steel piping sometimes used in the inhibited potable water systems. The advantage of using this steel was its availability in sheet form which made easy the machining of test coupons and its high reactivity with water. This made the steel suitable for the study of interactions between the aqueous solutions of hydraulic drag reducing agents and the corrosion inhibitors.

3. Inhibitors

Inhibitors were obtained from a number of North American suppliers. Those chosen for this study were selected based on their solubility in aqueous solutions of the friction reducing agents. The inhibitors used are summarized in Table 1.

Table 1

Inhibitors Included In This Study

Company	Inhibitor	Active Part of Inhibitor
Dearborn Co.	Dearborn 546	molybdate
Cortec Corporation	VCI-649 VCI-609	amine carboxylates ammonium salts
Alchem Inc.	Alchem 918 Alchem 936 Alchem 3E19 Alchem 3C85 Alchem 3C84	proprietary proprietary sodium tetraborate & molybdate sodium molybdate proprietary
Ideas Inc.	Ida-Freeze	amine complex
Alox Corporation	Aqualox 225A-100 Aqualox 232	amine salts proprietary
Calgon Corporation	TG-10 CL-50 MSC Plus	phosphate glass phosphates molybdate

B) Static Laboratory Immersion Testing

In the static tests, steel test coupons measuring 2 by 5 inches, degreased in acetone and ground to 400 grit by SiC paper using water as a lubricant, were submerged in an aqueous solution containing one of the friction reducing agents, an antifoaming agent and an inhibitor in a 1 L glass jar. The oxygen was removed from the solution with a compressed nitrogen gas purge before the jar was hermetically sealed. The test coupons in the glass jars were held at 30 degrees from the horizontal position during their exposure. Hermetically closed jars with their contents were held at a constant temperature of 20° for the time indicated in Table 2. The metal samples were inspected at the end of these tests by microscope for signs of pitting. The solutions were analyzed for iron by atomic absorption and spectrophotometrically so that quantitative information was obtained on the inhibition of steel corrosion.

The length of these tests varied from 2 to 4 months. Results are summarized in Table 2.

Table 2

Results of Immersion Tests at 20°C in Oxygen Free Friction Reducing Agent Solutions
Containing Inhibitor Dosages Recommended by Suppliers

Sample No	Test Duration (days)	Friction Reducing Agent	Inhibitor	Inhibitor Dosage	pH	Observations	
						Steel Coupon After the Test	Solution After the Test
1	101	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Dearborn 546	3.1 g/L	10.1	Small spots of surface rust, shiny	Small amount of ppt 0.41* mg Fe/L
2	101	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Cortec VCI-649	7.0 g/L	8.1	No pits, shiny	Small amount of ppt 0.69* mg Fe/L
3	101	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Cortec VCI-609	0.357 g/L	6.0	No pits, dull	Large amount of ppt 43.3* mg Fe/L
4	101	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Phosphate	1 ppm	4.9	No pits, dull	Large amount of ppt 0.55 mg Fe/L
5	101	Ethoquad, with 2,6-Dihydroxybenzoic Acid	None	-	4.8	No pits, dull spots	Large amount of ppt 50.0* mg Fe/L
6	80	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 936	9 ppm	6.7	No pits, dull	Large amount of ppt 3.30 mg Fe/L
7	80	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 918	9 ppm	6.7	No pits, dull	Large amount of ppt 5.75 mg Fe/L
8	12	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 3E19	10 ppm	6.5	No pits, dull	Large amount of ppt 7.65*
9	12	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 3C85	10 ppm	6.5	No pits, dull	Large amount of ppt 7.1*

* Results obtained by Atomic Absorption Analysis of the liquid. All other results obtained spectrophotometrically.

Table 2

Results of Immersion Tests at 20°C in Oxygen Free Friction Reducing Agent Solutions
Containing Inhibitor Dosages Recommended by Suppliers

Sample No	Test Duration (days)	Friction Reducing Agent	Inhibitor	Inhibitor Dosage	pH	Observations	
						Steel Coupon After the Test	Solution After the Test
10	80	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Ida Freeze	10 ppm	6.5	No pits, dull	Large amount of ppt 1.35 mg Fe/L
11	68	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 3E19	2000 ppm	9.9	Small amount of surface rust, shiny	Small amount of ppt 7.65* mg Fe/L
12	68	Ethoquad, with 2,6-Dihydroxybenzoic Acid	Alchem 3C85	150 ppm	8.7	No pits, shiny	Small amount of ppt 7.1* mg Fe/L
1A	101	Ethoquad, with 3-Methylsalicylic Acid	Dearborn 546	3.1 g/L	10.0	Spots of surface rust present, shiny	Small oil-like layer 0.31* mg Fe/L
2A	101	Ethoquad, with 3-Methylsalicylic Acid	Cortec VCI-649	7.0 g/L	8.1	No pits, shiny	Small oil-like layer 0.6* mg Fe/L
3A	101	Ethoquad, with 3-Methylsalicylic Acid	VCI-609	0.357 g/L	5.6	Pits present, dull	Small oil-like layer 0.25 mg Fe/L
4A	101	Ethoquad, with 3-Methylsalicylic Acid	Phosphate	1 ppm	4.9	Pits present, dull	Large amount of ppt 14.15 mg Fe/L
5A	101	Ethoquad, with 3-Methylsalicylic Acid	None	-	4.7	Pits present, dull	Large amount of ppt 149.00* mg Fe/L
6A	91	Ethoquad, with 3-Methylsalicylic Acid	Alchem 918	9 ppm		No pits, dull	Large amount of ppt 0.60 mg Fe/L

* Results obtained by Atomic Absorption Analysis of the liquid. All other results obtained spectrophotometrically.

Table 2

Results of Immersion Tests at 20°C in Oxygen Free Friction Reducing Agent Solutions
Containing Inhibitor Dosages Recommended by Suppliers

Sample No	Test Duration (days)	Friction Reducing Agent	Inhibitor	Inhibitor Dosage	pH	Observations	
						Steel Coupon After the Test	Solution After the Test
7A	91	Ethoquad, with 3-Methylsalicylic Acid	Alchem 936	9 ppm		Pits present, dull	Large amount of ppt 1.40 mg Fe/L
8A	23	Ethoquad, with 3-Methylsalicylic Acid	Alchem 3E19	10 ppm		No pits, shiny	Large oil-like layer 29.17*
9A	23	Ethoquad, with 3-Methylsalicylic Acid	Alchem 3C85	10 ppm	5.1	No pits, dull	Large oil-like layer 12.36*
10A	80	Ethoquad, with 3-Methylsalicylic Acid	Ida Freeze	10 ppm	6.8	No pits, dull spots	Large amount of ppt 2.40 mg Fe/L
11A	68	Ethoquad, with 3-Methylsalicylic Acid	Alchem 3E19	2000 ppm	9.0	No pits, shiny	Large amount of ppt 1.70 mg Fe/L
12A	68	Ethoquad, with 3-Methylsalicylic Acid	Alchem 3C85	150 ppm	7.7	No pits, shiny	Small amount of ppt small oil-like layer 2.25 mg Fe/L
13A	52	Ethoquad, with 3-Methylsalicylic Acid	Calgon CL50	100 ppm	7.1	Pits present, dull	Large amount of ppt small oil-like layer 0.67 mg Fe/L
14A	52	Ethoquad, with 3-Methylsalicylic Acid	Calgon TG-10	20 ppm	7.0	Pits present, dull	Small amount of ppt 0.45 mg Fe/L

* Results obtained by Atomic Absorption Analysis of the liquid. All other results obtained spectrophotometrically.

Table 2

Results of Immersion Tests at 20°C in Oxygen Free Friction Reducing Agent Solutions
Containing Inhibitor Dosages Recommended by Suppliers

Sample No	Test Duration (days)	Friction Reducing Agent	Inhibitor	Inhibitor Dosage	pH	Observations	
						Steel Coupon After the Test	Solution After the Test
15A	52	Ethoquad, with 3-Methylsalicylic Acid	Calgon MCS-plus	5000 ppm	9.2	No pits, shiny	Small amount of ppt 0.08* mg Fe/L
16A	62	Ethoquad, with 3-Methylsalicylic Acid	Alox 232	5000 ppm	7.3	No pits, shiny	Small oil-like layer 0.46* mg Fe/L
17A	52	Ethoquad, with 3-Methylsalicylic Acid	Alox 225A-100	7500 ppm	8.9	No pits, shiny	Clear solution, no ppt 0.17* mg Fe/L
18A	52	Ethoquad, with 3-Methylsalicylic Acid	Ida Freeze	1000 ppm	8.9	No pits, shiny	Clear solution, no ppt 0.08* mg Fe/L

* Results obtained by Atomic Absorption Analysis of the liquid. All other results obtained spectrophotometrically.

Results of exposure tests indicate that in systems containing the 3-methylsalicylic acid the best inhibitors of steel were Ida Freeze, Alox 225A-100 and VCI-649. The steel coupon in the system inhibited with Dearborn 546 showed signs of pitting. This may have been associated with the droplets of oily phase that separated from the system and were observed to settle on the upper surface of the test coupon during the test duration.

In the systems containing 2,6-dihydroxybenzoic acid the best inhibition of the steel coupon was achieved with VCI-649 and VCI-609 inhibitors. In the system incorporating the Dearborn 546 inhibitor, the steel surface appeared etched and slightly pitted. In this system droplets of oily phase were present indicating separation of the mixture on standing. The steel coupons in the system inhibited with VCI-649 were attacked by slight pitting.

C) Electrochemical Testing

Two electrochemical test methods were used to determine how effective the various corrosion inhibitors were in preventing corrosion of low carbon steel in environments incorporating one of the friction reducing agents. The two methods used were the measurement of electrode potentials and the polarization technique.

Corrosion Potential Measurement

Corrosion potential measurement provides an indication of the oxidizing power (i.e. aggressiveness) of an environment in which the steel specimen is exposed. Potential is a thermodynamic quantity and can be used to determine whether the reaction (i.e. corrosion) will occur spontaneously. However, it does not give information about the rate of reaction (i.e. corrosion rate).

Using the standard calomel electrode the galvanic series for the steel was determined in environments consisting of water, antifoaming agent, corrosion inhibitor, ethoquad and either 3-methylsalicylic acid (FRA # 1) or 2,6,-dihydroxybenzoic acid (FRA # 2). Data obtained at 23°C is summarized in Table 3. In this table the reactivity of the metal and the environment increases with the increasing negative potential.

Table 3

Drag Reducing Agent	Inhibitor	Other Additives	Open Circuit Potential E_{corr} (mV vs SCE)
Ethoquad + 3-methylsalicylic Acid	VCI-649	N_2	-270
Ethoquad + 3-methylsalicylic Acid	DB-546	N_2	-382
Ethoquad + 3-methylsalicylic Acid	Alchem 3C84	N_2	-532
Ethoquad + 3-methylsalicylic Acid	--------	N_2	-635
Ethoquad + 3-methylsalicylic Acid	VCI-609	N_2	-681
Ethoquad + 3-methylsalicylic Acid	VCI-609	O_2	-64
Ethoquad + 3-methylsalicylic Acid	VCI-649	O_2	-157
Ethoquad + 3-methylsalicylic Acid	Alchem 3C84	O_2	-164
Ethoquad + 3-methylsalicylic Acid	--------	O_2	-200
Ethoquad + 3-methylsalicylic Acid	DB-546	O_2	-262
Ethoquad + 3-methylsalicylic Acid	Alox 225A-100	N_2	-291
Ethoquad + 3-methylsalicylic Acid	Ida Freeze	N_2	-693
Ethoquad + 2,6-dihydroxybenzoic Acid	VCI-649	N_2	-282
Ethoquad + 2,6-dihydroxybenzoic Acid	DB-546	N_2	-345
Ethoquad + 2,6-dihydroxybenzoic Acid	Alchem 3C84	N_2	-585
Ethoquad + 2,6-dihydroxybenzoic Acid	--------	N_2	-620
Ethoquad + 2,6-dihydroxybenzoic Acid	VCI-609	N_2	-637
Ethoquad + 2,6-dihydroxybenzoic Acid	VCI-609	O_2	-125
Ethoquad + 2,6-dihydroxybenzoic Acid	VCI-649	O_2	-207
Ethoquad + 2,6-dihydroxybenzoic Acid	Alchem 3C84	O_2	-256
Ethoquad + 2,6-dihydroxybenzoic Acid	DB-546	O_2	-262
Ethoquad + 2,6-dihydroxybenzoic Acid	--------	O_2	-329

Results in Table 3 are divided into four subsections based on the type of friction reducing agent used and the environment under which the test was conducted. Each subsection is arranged according to the open circuit (i.e. corrosion) potentials from the most noble to the most active. The inhibitor VCI-649 was found to provide the most noble environment with either FRA # 1 or # 2 in all oxygen free systems, whereas VCI-609 gave the most noble results in an oxygen saturated environment with either FRA # 1 or FRA # 2. Overall the least active (i.e. most noble) system consisted of FRA # 1 (3-methylsalicylic acid) and the VCI-609 corrosion inhibitor in an oxygen enriched environment.

The potential versus time records in Figures 1 and 2 show variation in corrosion potentials with time in systems containing mixtures of water with ethoquad and 2,6-dihydroxybenzoic acid (FRA # 2) or 3-methylsalicylic acid (FRA # 1) along with different inhibitors and an antifoaming agent. It was observed that the corrosion potentials in systems containing VCI-649, DB-546 and A-3C84 shifted with time in a positive direction indicating ennoblement of the steel. A shift of up to 250 mV in corrosion potential was observed in the systems containing VCI-649 and DB-546 inhibitors, while in the system inhibited with A-3C84 only 100 mV shift in potential was observed. The shift in potentials was attributed to formation of a protective film on the surface of exposed steel samples.

Corrosion Rate Measurements

Electrochemically, corrosion rate measurement is based on the determination of the oxidation current at corrosion potential. The oxidation current is the same as the corrosion current, i_{corr}. Current has the units of coulombs per second. Coulombs are related to the weight of electroactive (corroding) material through Faraday's Law. Thus the corrosion current is related directly to corrosion rate. A Tafel Plot is performed to determine experimentally i_{corr}. The ranking of corrosive environment, in this case inhibitors performance, is made based on this current.

Testing is done on a free electrode system schematically represented in Figure 3. This system includes two separate electronic circuits. One of these, between the test and reference electrode is a voltage circuit. The other circuit passes (corrosion) current between the test electrode and the auxiliary (electrochemically inert) electrode.

A high impendence potentiostat polarizes the test electrode, controls the potential, adjusts it and measures the corrosion currents. During the actual testing one measures and plots current response as a function of applied over voltage. Since the corrosion currents usually vary over several decades, a semilogarithmic plot is used.

Tafel Plots were obtained for 1020 steel in both oxygen free and oxygen saturated aqueous liquids at 23°C containing a friction reducing agent, an antifoamant and a corrosion inhibitor. The concentrations of inhibitors used are those indicated in the fifth column of Table 2. Tafel Plots were not determined for all solutions listed in this table, rather only for those which showed stability and did not form a multiphase mixture during a short screening period of one day. The Tafel curves are summarized in Appendices I through IV.

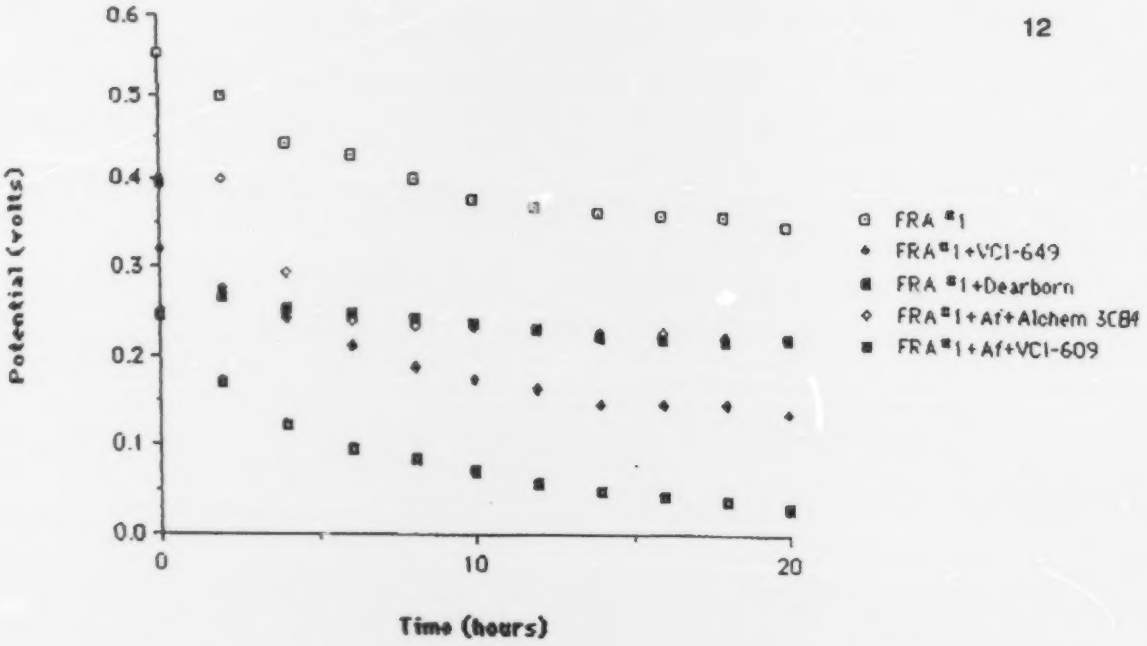


Figure 1 Variation in Steel Potential with Time (Measured Against Pt Electrode) for Systems Incorporating Ethoquad with 3-Methylsalicylic Acid (FRA # 1) and Various Corrosion Inhibitors in Absence of Oxygen, at 23°C

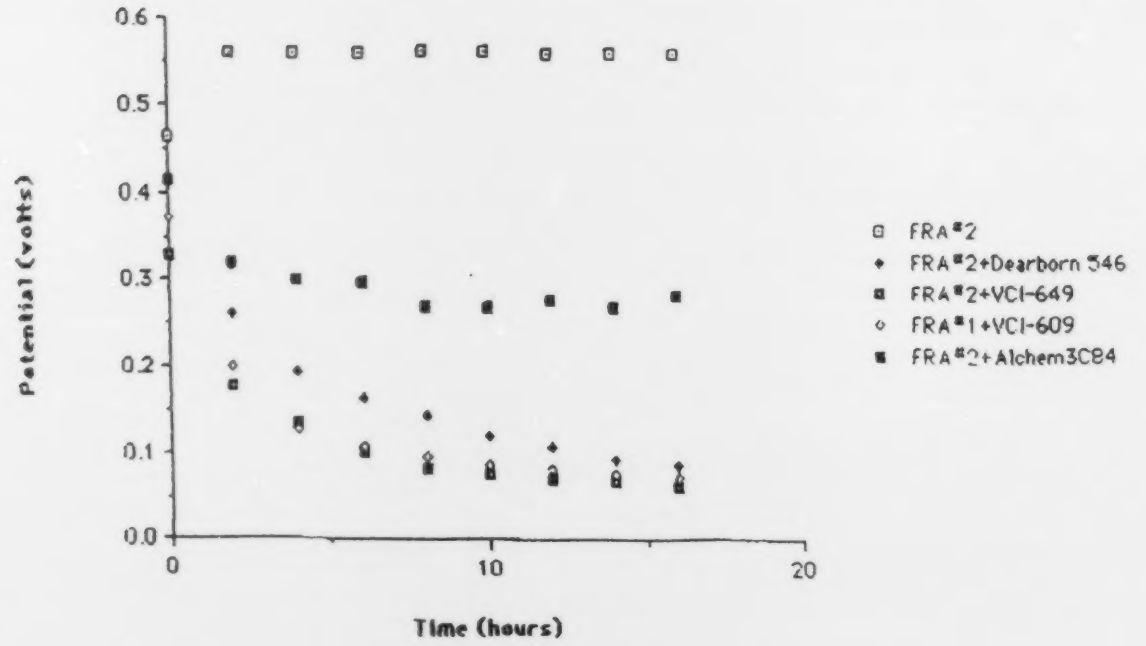
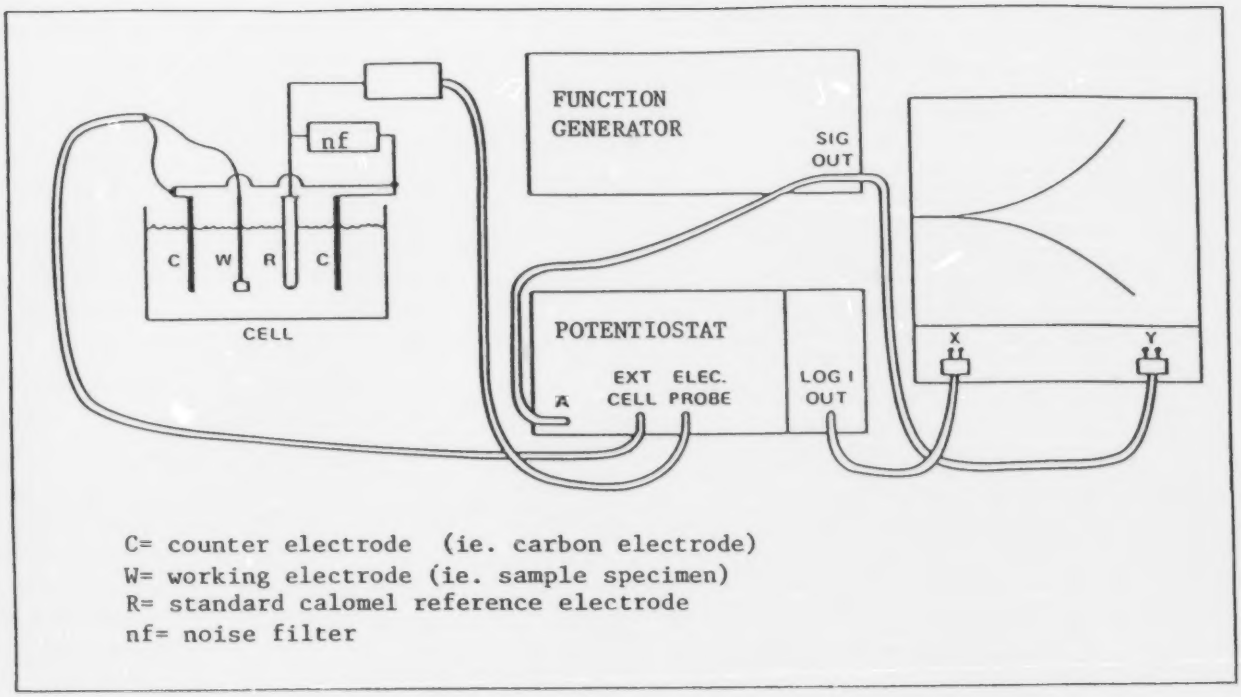


Figure 1 Variation in Steel Potential with Time (Measured Against Pt Electrode) for Systems Incorporating Ethoquad with 2,6-dihydroxybenzoic Acid (FRA # 2) and Various Corrosion Inhibitors in Absence of Oxygen, at 23°C



C= counter electrode (ie. carbon electrode)
W= working electrode (ie. sample specimen)
R= standard calomel reference electrode
nf= noise filter

Figure 3: INSTRUMENT SET-UP FOR TAFEL PLOTS.

The corrosion current density, which is proportional to corrosion rates, was determined for each liquid mixture from the intersection of its respective cathodic Tafel curve and corrosion potential. The values obtained for mixtures containing 3-methylsalicylic acid (FRA # 1) are summarized in Table 4 while those for mixtures with 2,6-dihydroxybenzoic acid (FRA # 2) are in Table 5. As the corrosion currents (which are proportional to corrosion rates) in Table 4 indicate, the corrosion rates in the systems that incorporate FRA # 1 are the same or lower in all oxygen saturated systems than in oxygen free systems. However, the corrosion rates of systems incorporating Ida Freeze and Alox 225A-100 inhibitors were determined only in the oxygen free systems so this statement does not apply to them. The corrosion rates are the highest for the uninhibited system. The best inhibitors of steel in this system was VCI-649 and Alox 225A-100. The VCI-649 and the Alox 225A-100 inhibitors, according to the data in Table 4, reduced the corrosion current of the steel in the deoxygenated tnad inhibited systems containing 3-methylsalicylic acid, ethoquad, and antifoamant and water to less than a few hundredths of those observed for the uninhibited system. In these systems, containing oxygen, DB-546 and VCI-649 inhibitors were the most effective while the Ida Freeze and the Alox 225A-100 inhibitors were not tested.

In the systems containing 2,6-dihydroxybenzoic acid it was again the VCI-649 and DB-546 inhibitors that performed the best. Oxygen introduction into the FRA # 1 system free of inhibitors caused some reduction in the corrosion current density, however according to the results of electrochemical testing conducted with systems containing the 2,6-dihydroxybenzoic acid in Table 5, the effect of oxygen appears less clear than in systems containing the 3-methylsalicylic acid. In these systems oxygen was both beneficial and detrimental to inhibition of the steel. As can be seen from data in Table 5, the presence of oxygen reduced the effectiveness of the VCI-609 and DB-546 inhibitors even though the corrosion rate in the oxygen saturated uninhibited 2,6-dihydroxybenzoic acid was about one half of that observed in the oxygen free system.

Table 4

Corrosion Current Densities Obtained from Tafel Plots in Appendices I and III

System	Inhibitor	Corrosion Current Density $\mu A/cm^2$	
		In Absence of Oxygen	In Oxygen Saturated System
FRA # 1	None	45	8.5
FRA # 1	VCI-609	12.5	1.05
FRA # 1	A-3C84	0.45	0.66
FRA # 1	DB-546	0.12	3.2×10^{-2}
FRA # 1	VCI-649	7×10^{-2}	3.7×10^{-2}
FRA # 1	Ida Freeze	0.38	Not Tested
FRA # 1	Alox 225A-100	3.710^{-2}	Not Tested

Table 5

Corrosion Current Densities Obtained from Tafel Plots in Appendices II and IV

System	Inhibitor	Corrosion Current Density $\mu A/cm^2$	
		In Absence of Oxygen	In Oxygen Saturated System
FRA # 2	None	4.5	8.2
FRA # 2	VCI-609	0.4	0.15
FRA # 2	A-3C84	1.1	1.7
FRA # 2	DB-546	9.6×10^{-2}	1.6×10^{-2}
FRA # 2	VCI-649	7.6×10^{-2}	0.17

From the results of electrochemical testing it was noted that:

1. All six inhibitors tested by the electrochemical method demonstrated some inhibition of corrosion in the steel. Inhibitors Ida Freeze, Alox 225A-100, DB-546 and VCI-649 were particularly effective in inhibiting corrosion of steel surfaces at 23°C in the fluids composed of water and drag reducing agents.

2. All fluids consisting of aqueous solutions of drag reducing agents and inhibitors that were tested were observed to foam unacceptably when purged with oxygen or nitrogen gases. Antifoamants were used to control this behaviour. It was not established whether the antifoamants altered effectiveness of the inhibitors or friction reducing agents. Approximately 10 g/l of GE antifoam 60 with 30% silicone solids was used as an antifoam additive in systems containing the 3-methylsalicylic acid. The Doro Corning 1520 20% antifoam emulsion was used in the amount of 10 g/l in all test systems containing 2,6-dihydroxybenzoic acid.

3. Corrosion current densities in the oxygen saturated FRA # 1 system were generally lower than in the oxygen free systems. They were lower in all inhibited systems also.

4. Corrosion current densities incorporating FRA # 2 were higher in the oxygen saturated than in the oxygen free systems. This resulted in some loss of inhibiting efficiency of VCI-609 and DB-546 inhibitors. However, the efficiency of the other two inhibitors tested, i.e. the 3C84 and VCI-649, increased with the addition of oxygen. The corrosion current density of steel in the oxygen saturated and DB-546 or A-3C84 inhibited solution of ethoquad with 3-methylsalicylic acid was up to 6 times that in the oxygen free systems.

5. There was evidence of two-phase separation in all the FRA # 1 systems containing 3-methylsalicylic acid. The separation was also observed in the water-FRA # 1 mixtures that had no inhibitor and no antifoaming agent added to them. An oily phase came out of the FRA # 1 mixtures that incorporated DB-546 inhibitor.

6. Generally, solutions incorporating 2,6-dihydroxybenzoic acid (FRA # 2 systems) were more stable under all test conditions, than solutions incorporating the 3-methylsalicylic acid (FRA # 1 systems).

7. There was ennoblement of 100 to 300 mV in the corrosion potential in the FRA # 1 systems inhibited by the following inhibitors: VCI-649, DB-546, 3C84 and Alox 225A-100.

8. There was about 300 mV ennoblement of corrosion potential in the FRA # 2 systems inhibited by the following inhibitors: VCI-649 and DB-546.

9. Shift of potentials on the E vs time graphs towards more positive values may be beneficial, but also may bring the metal closer to pitting potential and increase the probability of pitting, especially if chlorides are present in the system. Anodic polarization curves could help to identify the tendency of these systems to pitting. From the anodic curves the breakdown potential could be determined and the reliability of the inhibitors could be assessed in terms of potential difference between steady state corrosion potential and this breakdown potential.

CONCLUSIONS

- The electrochemical tests were carried out on 6 inhibitors only. The static immersion tests were carried out on 14 inhibitors.
- Both test methods identified the VCI-649 inhibitor to be the most effective for the oxygen free systems containing either the 3-methylsalicylic acid or 2,6-dihydroxybenzoic acid.
- Both test methods indentified Alox 225A-100 and Ida Freeze as efficient inhibitors of steel in oxygen free systems of 3-methylsalicylic acid. These inhibitors have not been tested in oxygen saturated systems.
- The electrochemical method identified the VCI-649 inhibitor to be equally effective in the oxygen saturated and oxygen free cooling media incorporating 3-methylsalicylic acid.
- The immersion tests in oxygen saturated systems were not carried out in this study.
- Current electrochemical tests indicate that the corrosion rates of steel were reduced more than 50 times when VCI-649, Ida Freeze, Alox 225A-100 and DB-546 inhibitors were incorporated into the cool energy transfer media with either drag reducing agent.
- Electrochemical tests identified the Dearborn 546 inhibitor as the effective inhibitor of steel in systems with either 3-methylsalicylic acid or 2,6-dihydroxybenzoic acid in both oxygen free and oxygen saturated solutions. However, as the immersion tests revealed under stagnant conditions the inhibited mixture may separate into two phases. This could lead to pitting of the steel.
- An excellent performance during the immersion tests was also observed in systems of 3-methylsalicylic acid inhibited with Alox 225A-100 and Ida Freeze. This was indicated by shiny unattacked surfaces of steel test coupons and a stable one phase cooling medium at the end of test exposure. Neither of these systems was tested electrochemically in the oxygen saturated systems.
- The ethoquad, 3-methylsalicylic acid aqueous solutions of pH 4.1 to 4.8 are not very stable. They separate on standing into two phases. This separation into phases was observed also in the absence of inhibitors and the antifoaming agents.

RECOMMENDATIONS

The ethoquad, 3-methylsalicylic acid aqueous solutions of pH 4.1 to 4.8 are not very stable. They separate on standing into two phases. The separation of phases is not affected by the presence of inhibitors or antifoamants.

In the systems for which these cold energy transfer medium are intended, the prevalent problems will most probably be the flow induced corrosion. Therefore, further selection of corrosion protection additives requires test methods that provide relevant and predictive results. Even here, however, if for example, the intensity of flow in the pipes is lower than in the field an inhibitor that performed well in a test may not be effective in service. Therefore the regimes of flow must be exactly modeled. The experimental conditions for such tests must be selected to be service relevant and give corrosion attacks in an absence of inhibitors of the same type and magnitude as those in the field. Flow loop testing is recommended. Only such a test can simulate the regimes of flow service tubes. The flow loop apparatus is very sophisticated and experiments are costly and time consuming.

Also, there are potential problems associated with the biological activity in the systems containing the nitrogen containing ethoquad. The biofouling can lead to enormous service problems by releasing ferric ions, changing pH and formation of voluminous deposits.

We suggest a concerted effort be made by:

(1) Dr. John Young of Saint Mary's University to stabilize the ethoquad methylsalicylic acid - water mixtures.

(2) T. Betancourt to carry out further electrochemical work that will include:

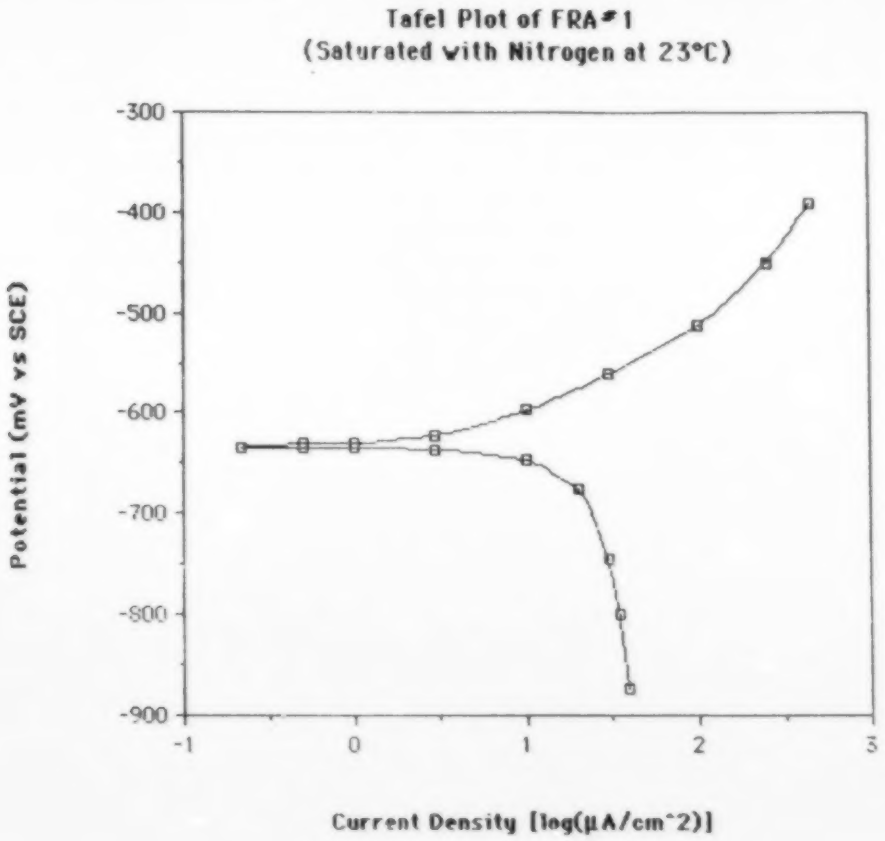
- determination of Tafel curves in both oxygen free and oxygen saturated systems with 3-methylsalicylic acid and Alox 225A-100 and Ida Freeze inhibitors,
- measurement of anodic polarization curves in oxygen free and oxygen saturated systems of 3-methylsalicylic acid incorporating VCI-649, 3C84, Alox 225A-100 and Ida Freeze inhibitors to determine pitting tendency,
- carry out the immersion tests in oxygen saturated systems of both the 3-methylsalicylic acid and 2,6-dihydroxybenzoic acid inhibited with DB-546, 3C84, VCI-649, Alox 225A-100 and Ida Freeze,
- carry out the immersion test in oxygen free systems of 3-methylsalicylic acid and 2,6-dihydroxybenzoic acid incorporating 3C84 inhibitor,
- do a similar test at elevated temperature.

(3) Dr. John Young and Terezia Betancourt of NSRFC to design and build the corrosion test loop system and to determine the reliability of selected inhibitors in service systems.

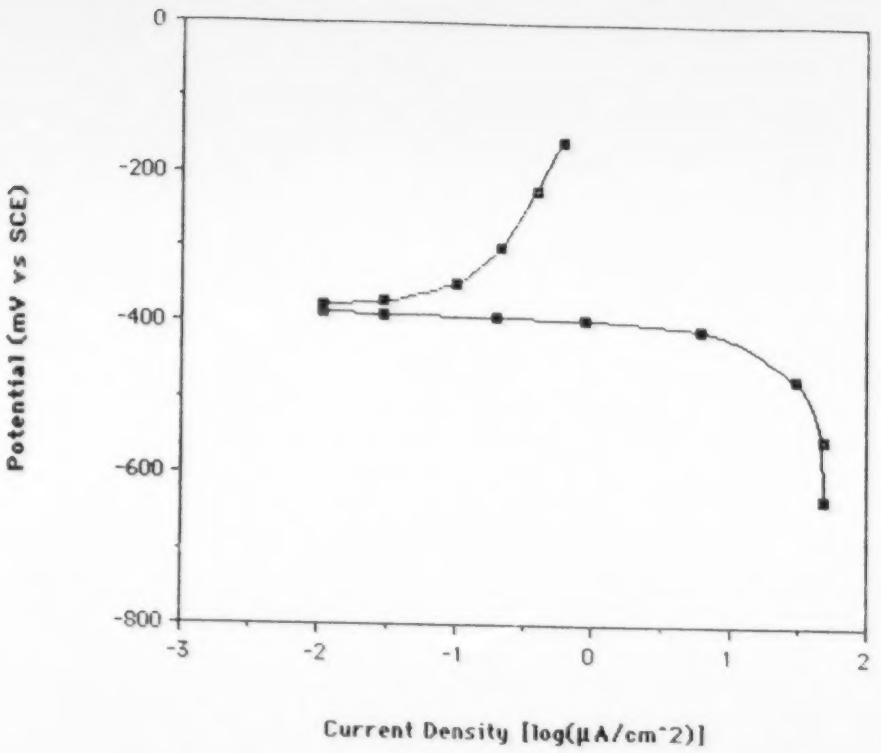
(4) Dr. Klaus Hellenbrand of NSRFC or other specialist in this field to design a suitable biocide system that would be compatible and acceptable for the ice water slurry systems incorporating drag reducing agents and the selected inhibitors.

APPENDIX I

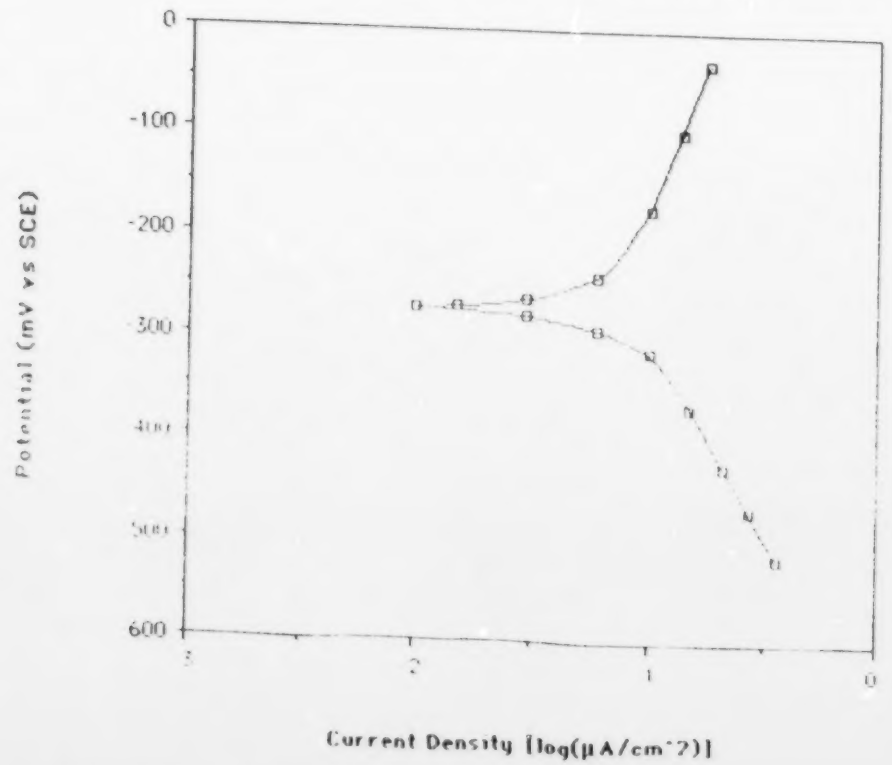
Tafel Plots for AISI 1020 steel in oxygen free FRA # 1 (3-methylsalicylic acid) media at 23°C with various inhibitors.



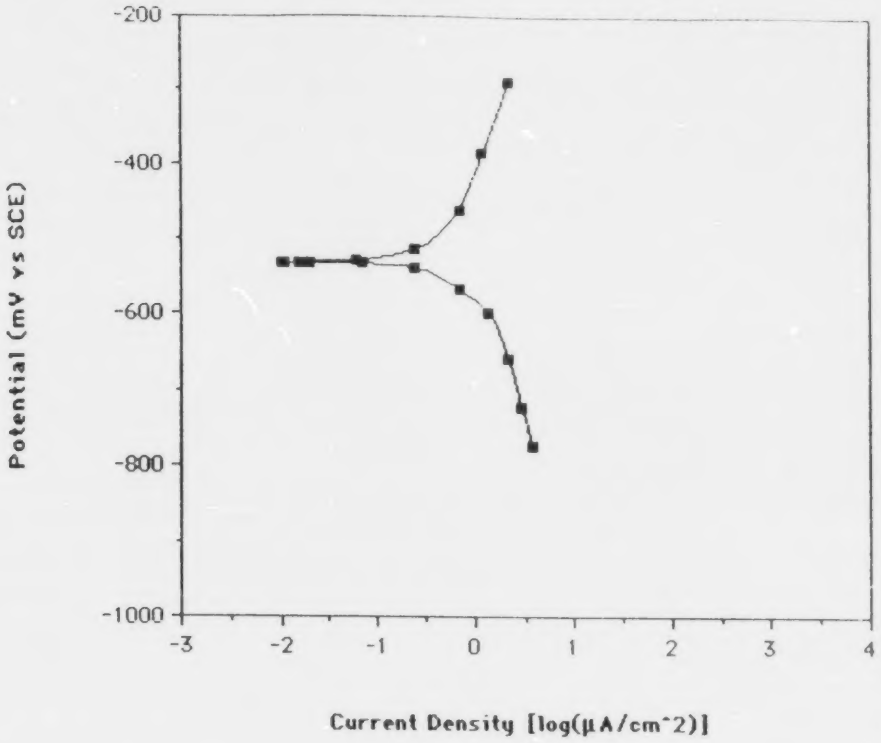
Tafel Plot of FRA#1 + Db 546
(Saturated with Nitrogen at 23°C)



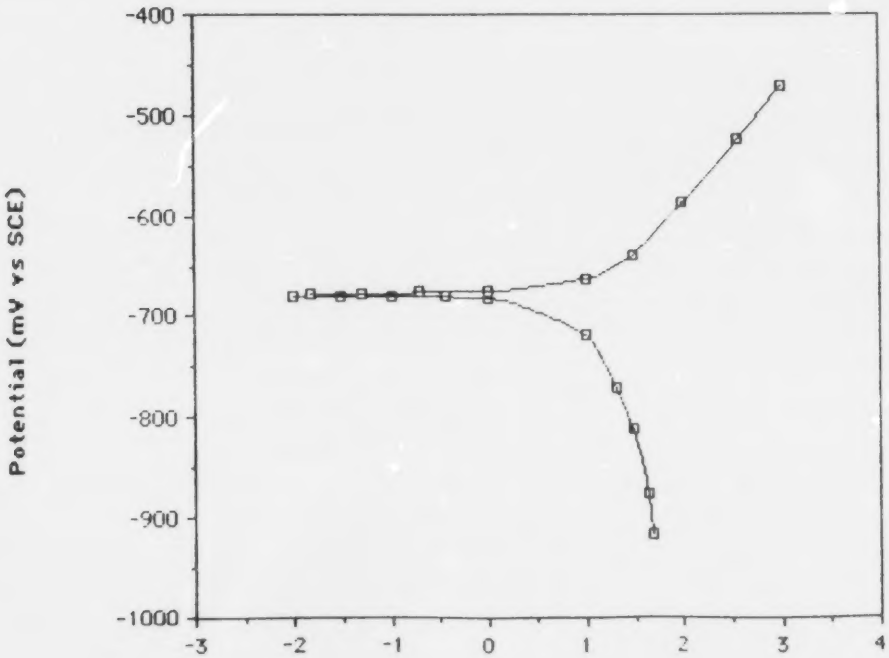
Tafel Plot of FRA#1 + YCI-649
(Saturated with Nitrogen at 23°C)



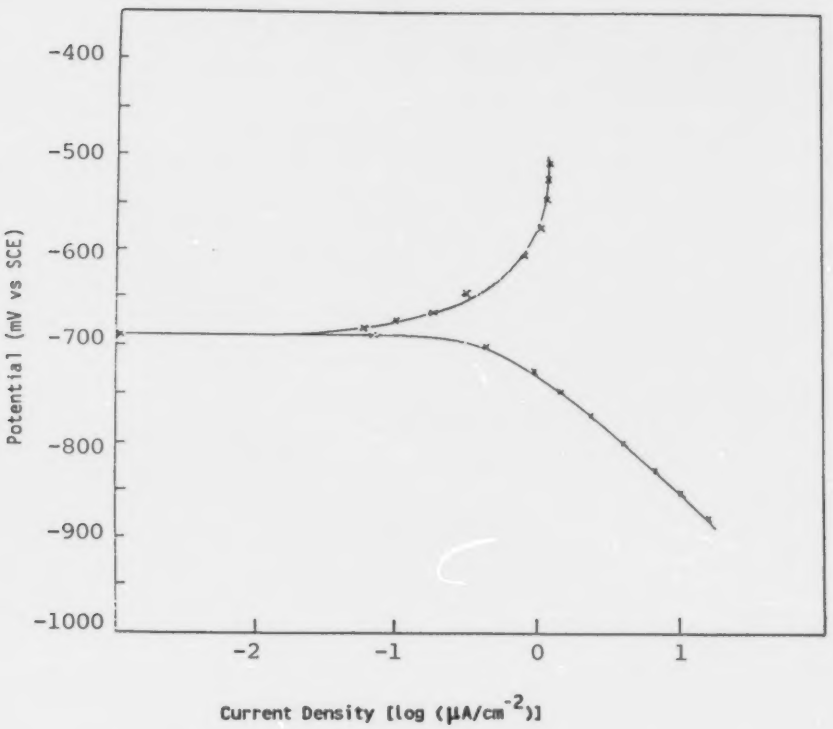
Tafel Plot of FRA#1 + 3C84
(Saturated with Nitrogen at 23°C)



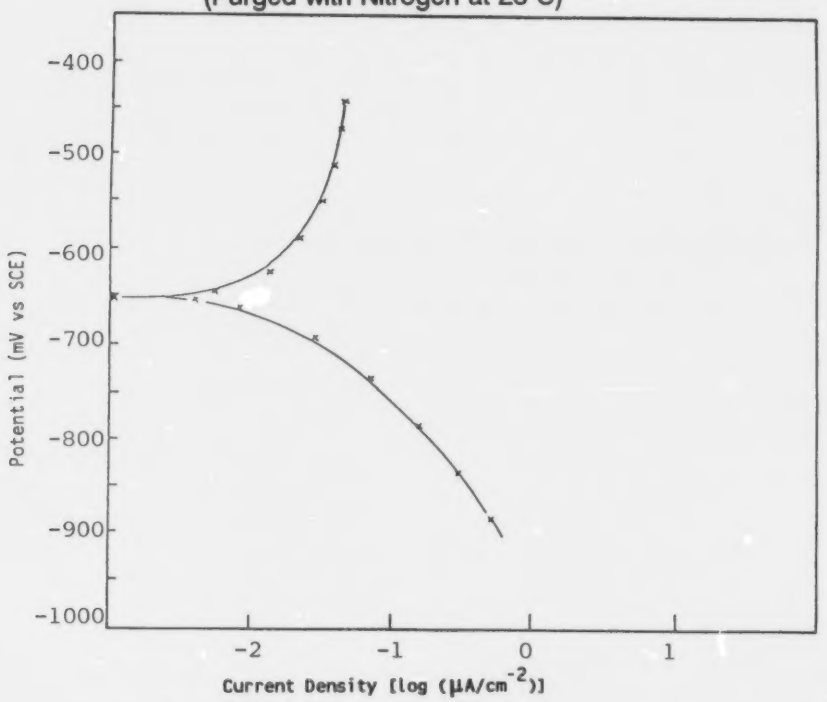
Tafel Plot of FRA#1 + YCI-609
(Saturated with Nitrogen at 23°C)



Tafel Plot of Steel in FRA # 1 + Ida Freeze
(Purged with Nitrogen at 23°C)

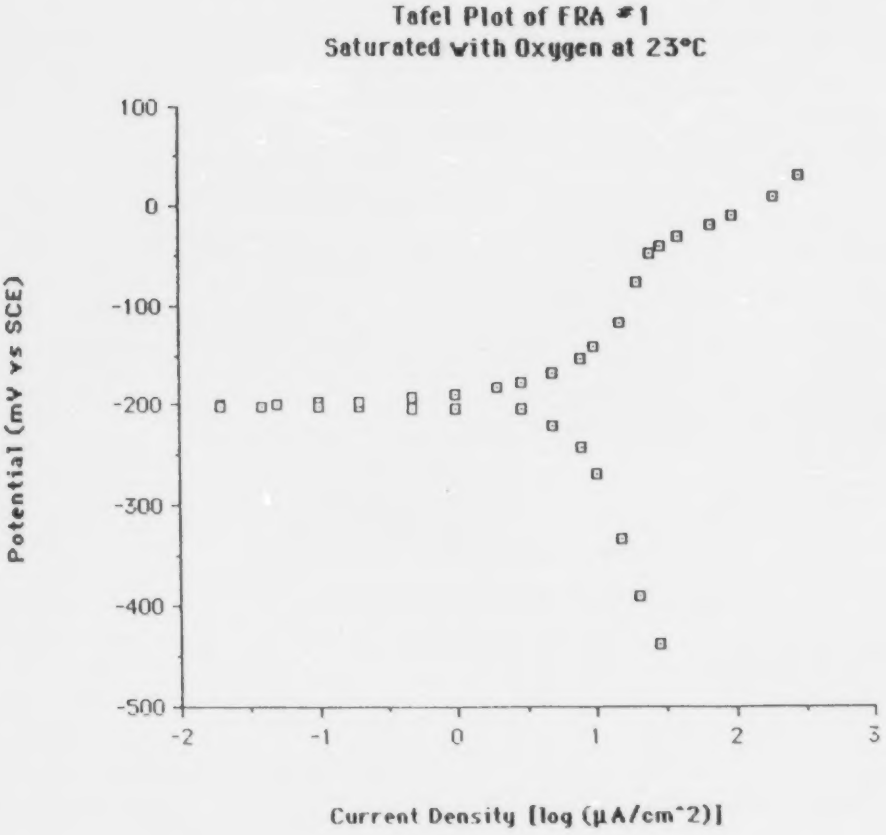


Tafel Plot of Steel in FRA # 1 + Alox 225A-100
(Purged with Nitrogen at 23°C)

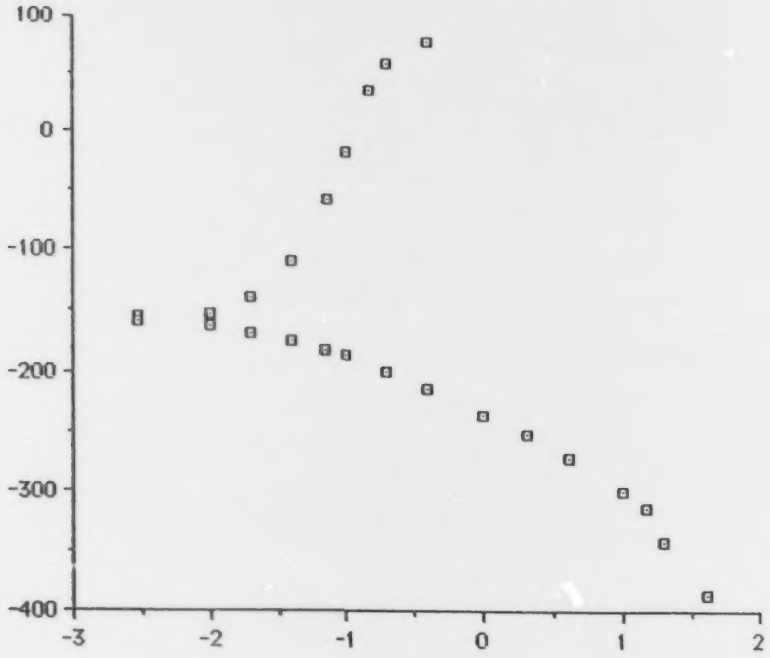


APPENDIX II

Tafel Plots for AISI 1020 steel in oxygen saturated FRA # 1 (3-methylsalicylic acid) media at 23°C with various inhibitors

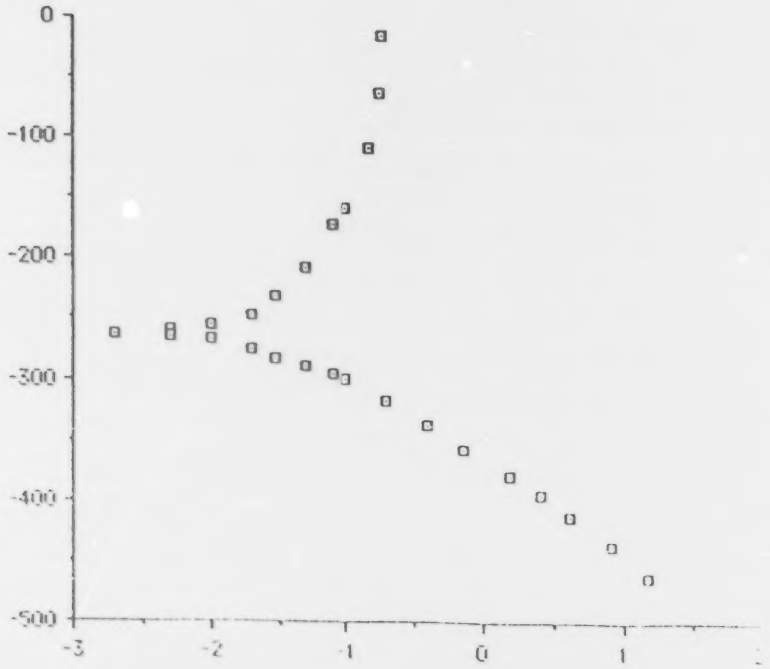


Tafel Plot of FRA #1 + YCI-649
Saturated with Oxygen at 23°C



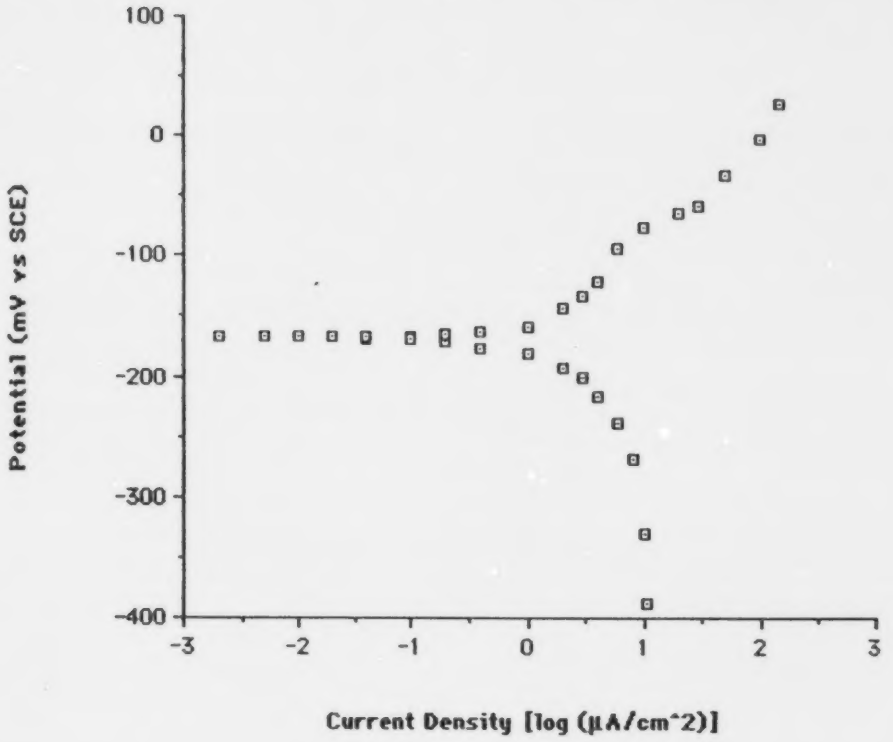
Current Density [log (μA/cm^2)]

Tafel Plot of FRA #1 + Dearborn 546
Saturated with Oxygen at 23°C

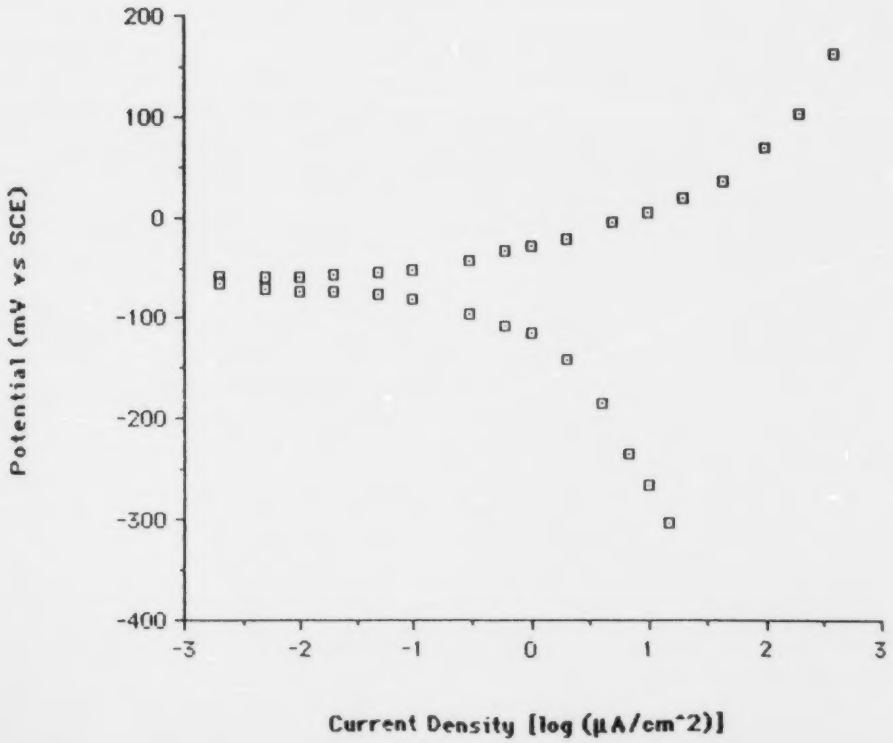


Current Density [log (μA/cm^2)]

Tafel Plot of FRA #1 + Alchem 3C84
Saturated with Oxygen at 23°C

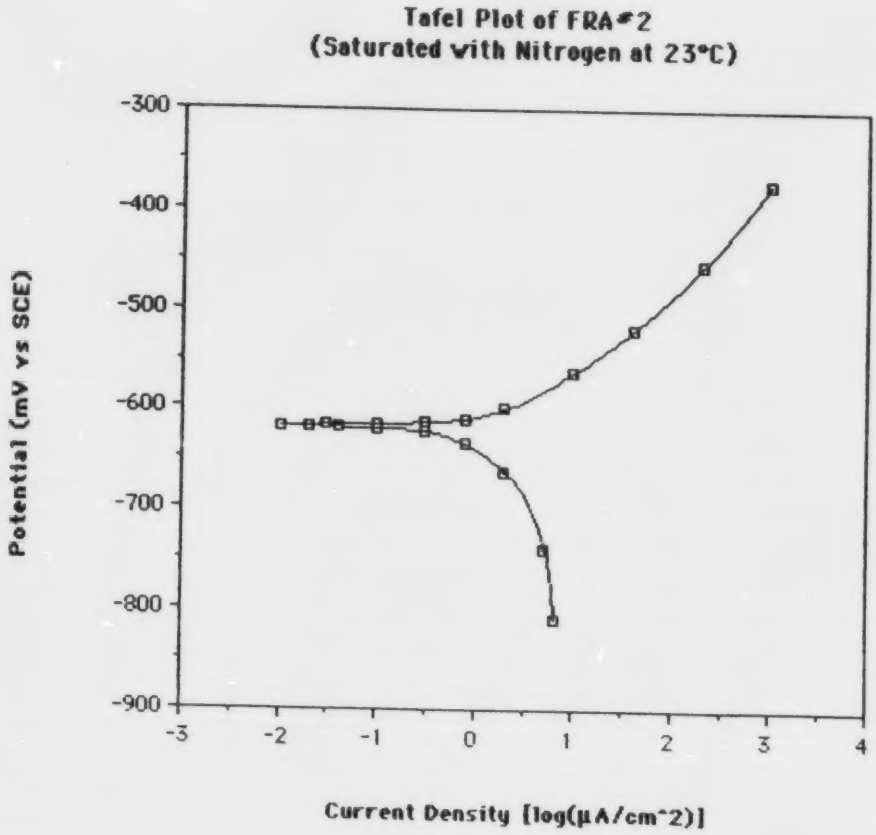


Tafel Plot of FRA #1 + YCI-609
Saturated with Oxygen at 23°C

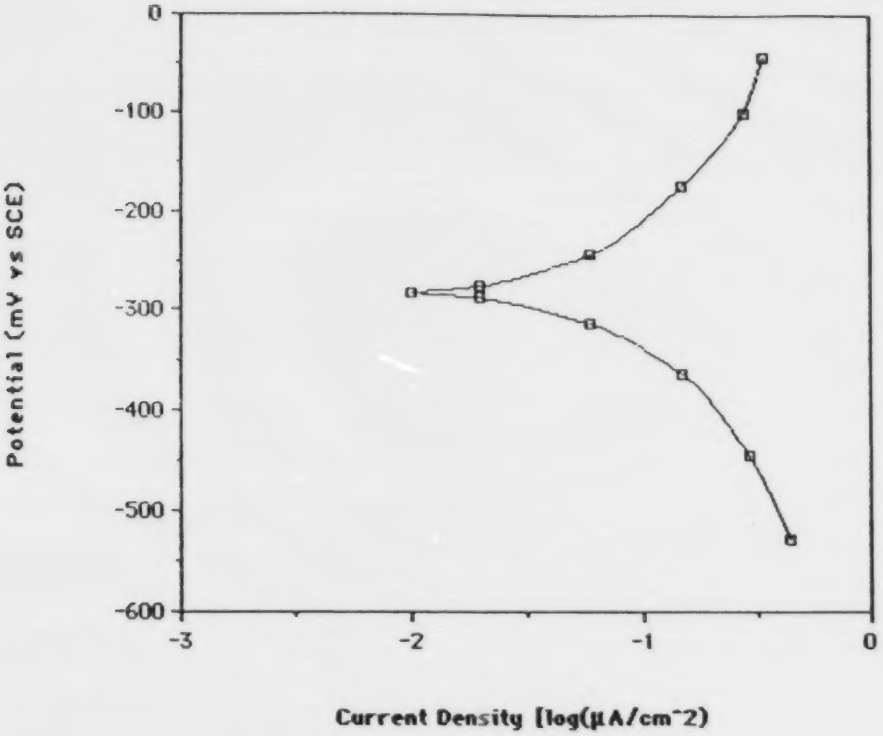


APPENDIX III

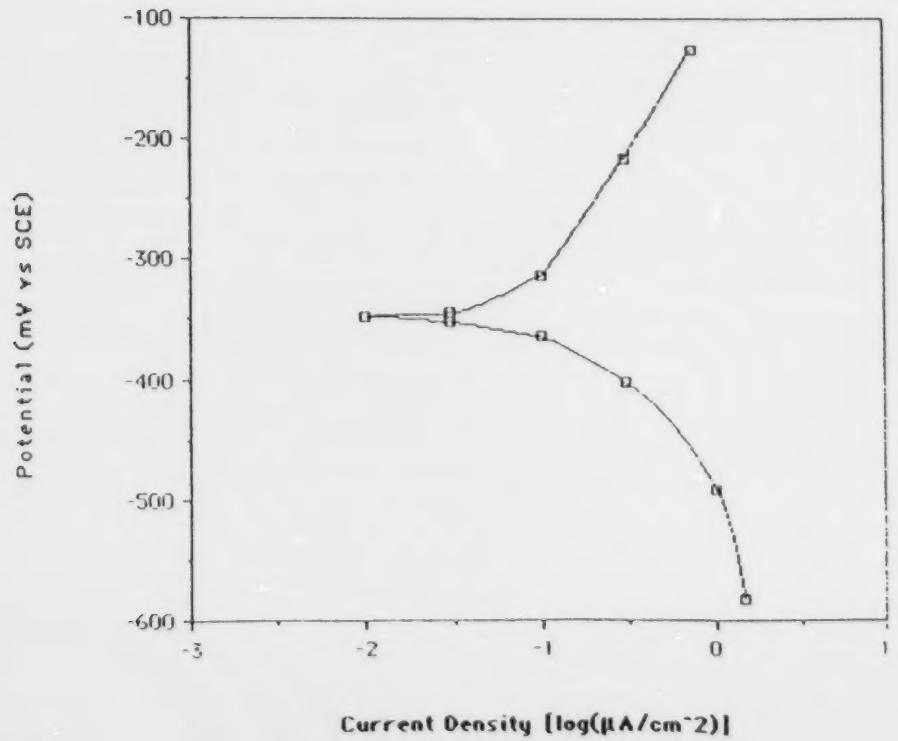
Tafel Plots for AISI 1020 steel in oxygen free FRA # 2 (2,6-dihydroxybenzoic acid) media at 23°C with various inhibitors.



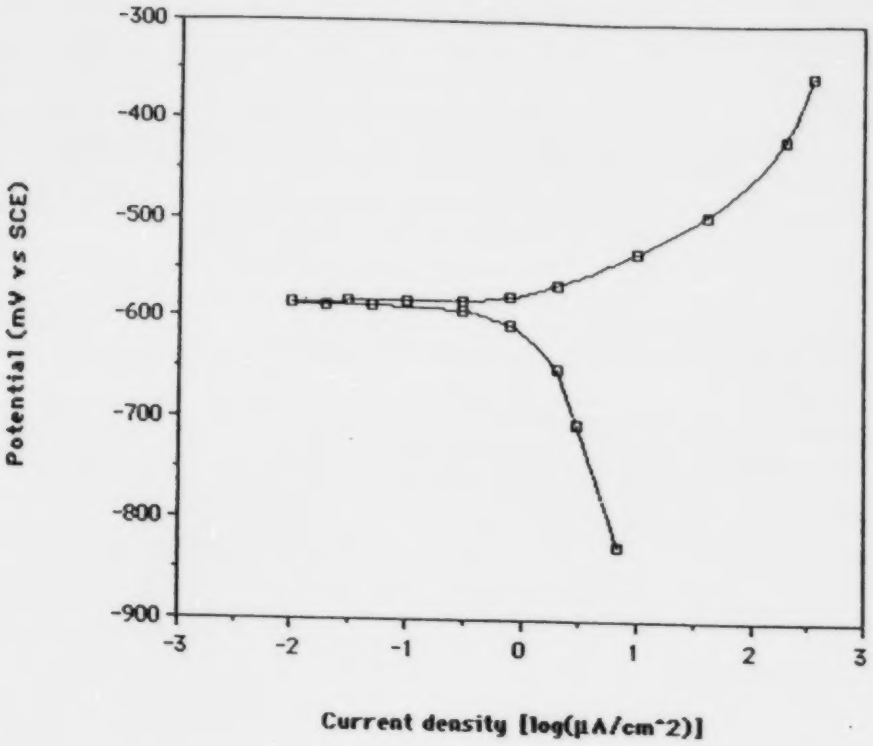
Tafel Plot of FRA#2 + YCI-649
(Saturated with Nitrogen at 23°C)



Tafel Plot of FRA#2 + Db 546
(Saturated with Nitrogen at 23°C)

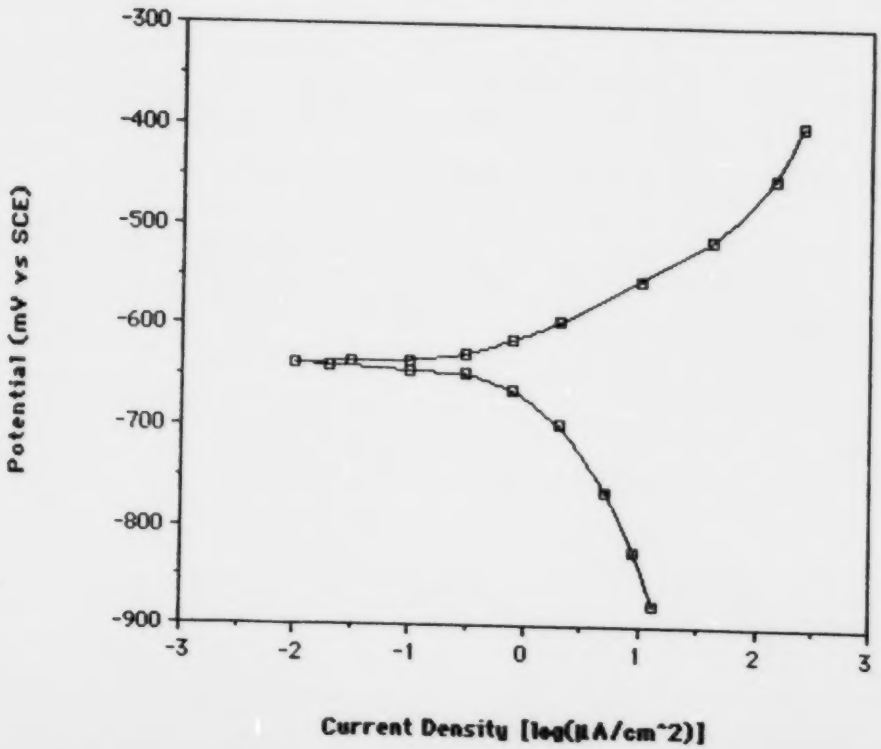


Tafel Plot of FRA#2 + 3C84
(Saturated with Nitrogen at 23°C)



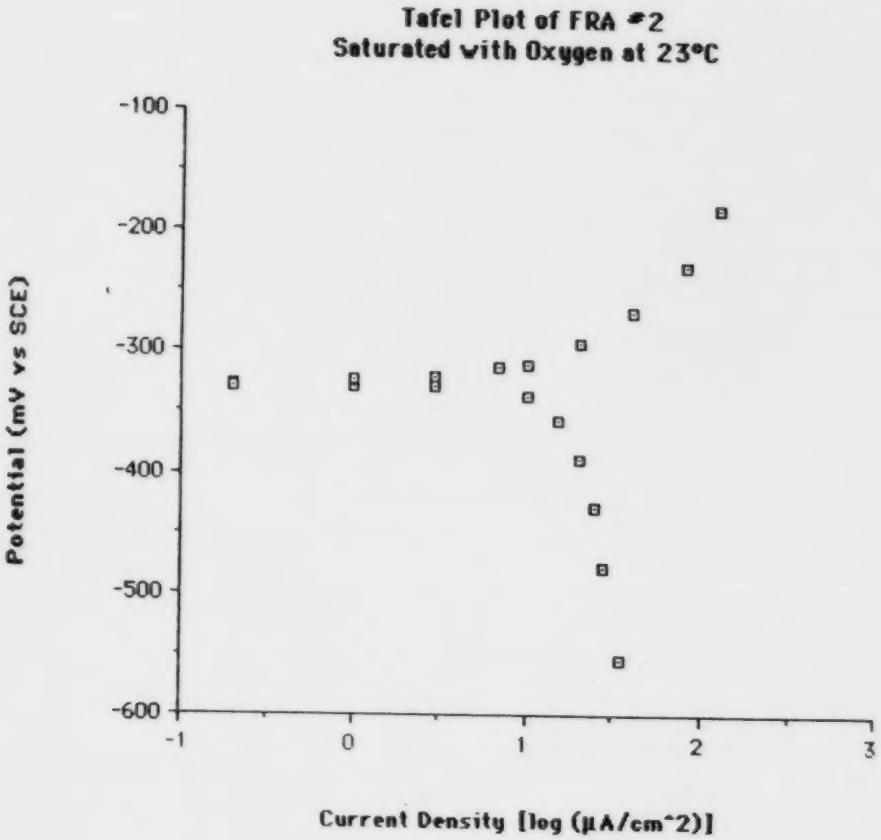
Current Density [log(µA/cm^2)]

Tafel Plot of FRA#2 + YCI-609
(Saturated with Nitrogen at 23°C)

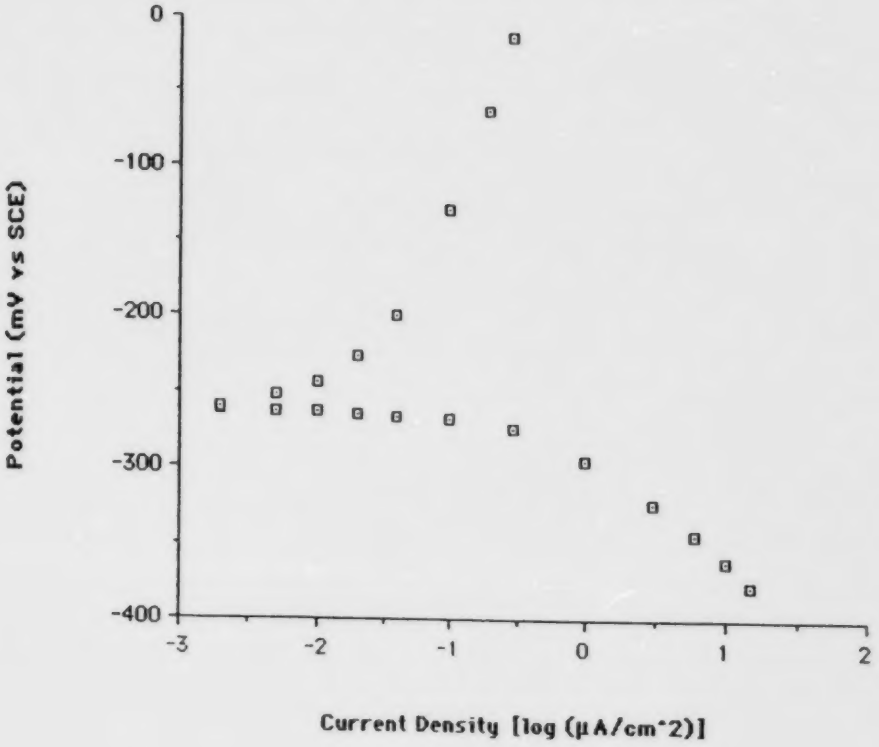


APPENDIX IV

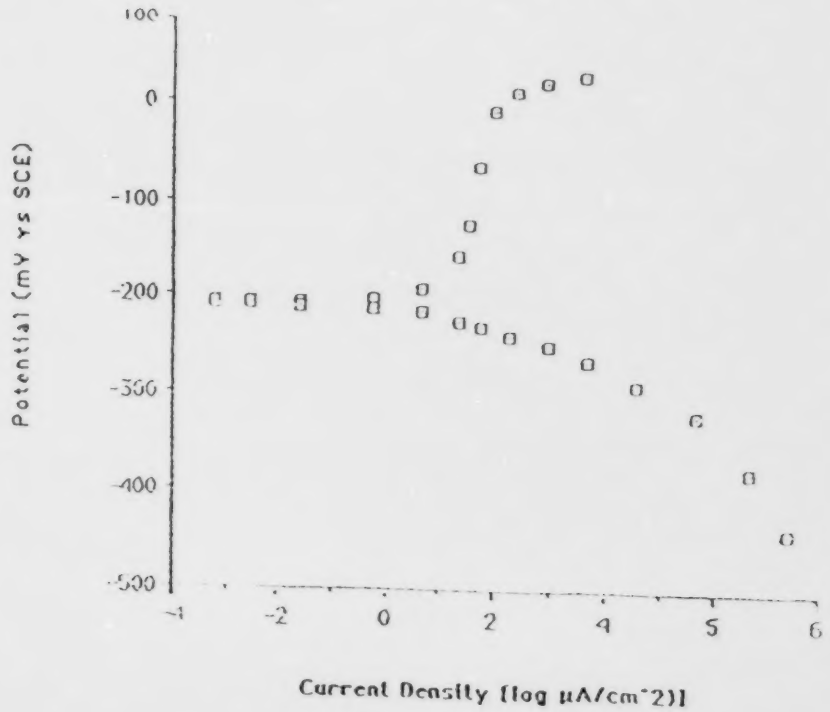
Tafel Plots for AISI 1020 steel in oxygen saturated FRA # 2 (2,6-dihydroxybenzoic acid) media at 23°C with various inhibitors.



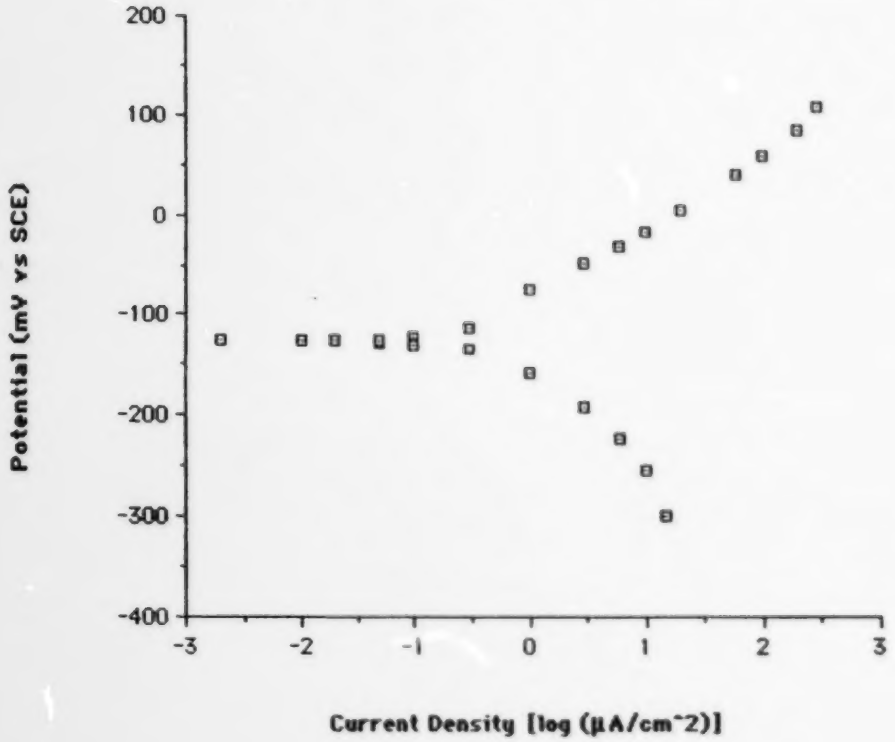
Tafel Plot Of FRA #2 + Dearborn 546
Saturated with Oxygen at 23°C



Tafel Plot of FRA #2 + VCI-649
Saturated with Oxygen at 23°C



Tafel Plot of FRA #2 + YCI-609 + AF
Saturated with Oxygen at 23°C



Tafel Plot of FRA #2 + 3C84
Saturated with Oxygen at 23°C